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16. ABSTRACT

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Impact of Tubificid Oligochaetes on Pollutant Transport in Bottom Sediments

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■ Pollutant transport in bottom sediments effected by tubificid oligochaetes was studied in laboratory microcosms. Tubificids burrow in surfacial sediments (typically 6–10 cm), ingest sediment fines (silt and clay particles), and egest them at the sediment/water interface as sand-sized fecal pellets. Sorbed pollutants are transported by default in this process irrespective of the relative pollutant fugacities in the system. For the compounds studied (hexachlorobenzene, pentachlorobenzene, and trifluralin), more than 90% of the chemicals contained in the biologically worked zone were transported to the sediment surface via this process during a 30–50-day period. Pollutant release into the water column was not comparably enhanced, which showed a 4–6-fold increase (over a 90-day period) in the presence of the worms. Pollutant release from intact fecal pellets was highly retarded by sorption. During a typical pellet residence time at the sediment surface (1–3 days), less than 20% of the pollutant contained in the pellet was released. Pollutant entrainment in fecal material further emphasizes the intimate link between benthic organisms and pollutant transport and fate in bottom sediments.

Introduction

Bottom sediments potentially constitute an important sink and/or source for aquatic pollutants. The direction of chemical movement across the sediment/water interface depends upon the relative fugacities of pollutant in the bottom sediment vs. the water column—with pollutant moving in the direction of lower fugacity (*1*, *2*). In this respect pollutant sorption to sediments is most important because sorption serves to lower pollutant fugacity and thereby increase the sink potential of bottom sediments for the more highly sorbed chemicals. It is not surprising, therefore, that bottom sediment is the eventual sink for many hydrophobic environmental contaminants.

The rate of chemical movement across the bottom sediment interface generally varies directly with the magnitude of pollutant fugacity difference between the sediment and water column, but the kinetic coefficient is highly dependent upon the actual exchange process(es) effecting the transport. In those aquatic systems where the bottom sediments are not subject to frequent resuspension, interfacial pollutant transport is generally rate controlled by chemical transport within the bottom, either in pore water or "piggybacked" on transported sediment particles. For hydrophobic pollutants, movement in pore water is highly retarded by sorption. For example, the kinetic coefficient for movement involving advection or dispersion is roughly reciprocally related to the sorption partition coefficient, K_p. If the partition coefficient is 10^4, the rate of chemical movement via pore water is attenuated 4 orders of magnitude, relative to a "nonsorbed" chemical species. Thus, for these types of chemicals, transport in the sorbed state (via sediment transport) may become quite significant.

Again, in those aquatic systems where the sediments are not subject to frequent resuspension, sediment reworking is largely the result of the activities of aquatic organisms (burrowing organisms and dimersal fishes). In freshwater systems, due to their trophic type, life habit, widespread distribution, and population densities, tubificid oligochaetes have the greatest potential for reworking surfacial sediments (*3*, *4*). In this study the transport of three hydrophobic pollutants (trifluralin, pentachlorobenzene, and hexachlorobenzene) in bottom sediments was investigated in small laboratory microcosms in the presence of tubificid oligochaetes. Behavior in these systems was contrasted with chemical transport in the absence of oligochaetes where molecular diffusion was the only operative transport process. Special emphasis was placed on elucidating the role of pollutant sorption in the transport process.

Experimental Section

Tubificid worms (>90% *Limnodrilus hoffmeisteri*, <10% *Tubifex tubifex*) were collected with their native sediment (largely fecal material) from Calls Creek, a small north Georgia stream draining predominantly undeveloped rural lands. In the laboratory the worms were placed in small open-air aquaria (sediment depth 5–10 cm) to allow the worms to recover and establish a fecal layer. Temperature and dissolved oxygen were maintained near field conditions, determined at the time of worm collection. Temperatures ranged from 15 to 20 °C at different collection times, with dissolved oxygen levels near saturation in each case. Larger quantities of whole sediment were collected from the same stream, air dried, and stored for brief periods (less than 30 days) prior to use. The "behavior" of processed sediments in these experiments was contrasted with fresh sediments (i.e., used immediately after collection) and found to be indistinguishable). These sediments were high in sand (50–80%) with organic carbon content varying from 0.5 to 1.5%. The fine fraction of the sediments (<50 μm) was fairly uniform in both organic carbon content (2.5–3.0%) and clay content (40–60%, largely kaolinite). Reagent-grade pentachlorobenzene and hexachlorobenzene (K and K Laboratories) and trifluralin (analytical reference standard, U.S. Environmental Protection Agency, Research Triangle Park, NC were used as received.

Sorption Equilibration of Test Chemicals. Pentachlorobenzene (pcb), hexachlorobenzene (hcb), and trifluoralin (tfn) were plated out of isooctane standard solutions (5–10 mg of each chemical) onto the walls of 40-L glass carboys. Air-dried whole sediment (6–10 kg) and distilled water (≈20 L) were added and the suspensions stirred until sorption equilibrium was achieved (at least 3 weeks).

Microcosm Setup. Portions of the whole sediment (≈1 kg dry weight), which had been previously equilibrated with the test chemicals, were transferred to 4-L flat-bottomed glass bottles (≈250-cm^2 cross-sectional area). Tubificid worms, which were removed from the incubation aquaria via air suction of small volumes of fecal material, were introduced into the microcosms and the containers slowly agitated to distribute the worms in the sediment. The containers were then placed on their sides, allowing the sediments to settle (≈5 min), and slowly righted to produce a fairly uniform sediment profile. The overlying water (and suspended solids) was siphoned off to within a centimeter of the sediment surface and replaced with distilled water. The microcosms were equipped with glass frits and resin traps (Figure 1) and air purge initiated. Air

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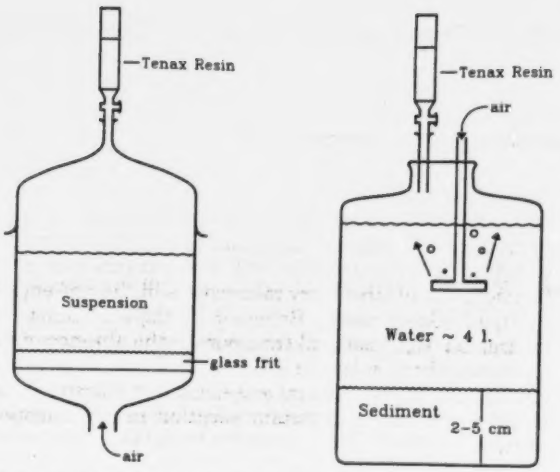

Figure 1. Microcosm and purge cell setup.

purge (≈0.8 L/min, directed upward so as not to resuspend bottom sediment) maintained the dissolved oxygen (d.o.) level in the aqueous phase near saturation (approximating field levels at the collection site). The collection and measurement of test chemicals sparged from the water column provided a direct quantification of the rates of chemical release from the bottom sediment. "Blank" microcosms were prepared in the same manner, excluding worms, to provide a contrast to worm-mediated pollutant transport.

Tubificid Activity. Although a conscious effort was made to maintain in the laboratory a sediment worm environment (i.e., d.o., temperature, sediment composition) similar to their native habitat, no comparison of organism activity in the field vs. the laboratory was made. Those aspects of worm activity deemed important to pollutant transport (i.e., sediment transport and restructuring) were monitored, and the resultant impact on pollutant movement was determined.

Tubificid Population. The worm density (i.e., worms per unit volume) in the fecal material used for microcosm spiking was determined by subsampling and enumeration (at least three samples). Target populations, which ranged from 100 to 5000 worms per microcosm, were then gauged by the volume of the spike. The coefficient of variation (standard deviation per mean) for multiple sampling of a given "spiking medium" was less than 0.3 in all cases. Upon termination of each experiment, the entire population was isolated (wet sieving, 60 mesh), counted, and characterized. For the higher populations, worm enumeration on small cores (≈1-cm^2 cross section) taken from the microcosm fecal layer were used to assess population stability and viability during the experiment. No counting statistics were determined on these cores. It was found that, for local sediments, "stable" tubificid populations could be maintained at population levels of 10^4–10^5 individuals/m^2 for a 90–100-day experimental period (with no added nutrients).

Sediment Transport. During fecal layer creation, sediment profile definition (i.e., depth of worm penetration and fecal layer depth) was monitored on the exterior wall of each microcosm. Depth measurements were taken at 2-day intervals on six equally spaced vertical transects of the sediment profile. Sediment transport during this period could be equated with fecal layer accumulation.

In addition, glass beads (125 μm, coated with fluorescent paints) were sprinkled on the sediment surface at roughly 30-day intervals. Black light was used to aid in bead observation, and variable color coding was used to differentiate times of introduction. Bead burial rates (from which sediment transport was inferred) were expressed in terms of burial depths on the exterior of the microcosms. The temporal and spatial frequency for bead depth measurements was the same as for strata formation described previously. At tubificid populations of 10^4–10^5 individuals/m^2, organism activity appeared uniform across the sediment surface. The coefficient of variation of depth measurements (fecal layer accumulation and/or bead burial) taken on different vertical transects was less than 0.4 in all cases, but generally less than 0.1. Also, bead disappearance from the surface appeared uniform across the microcosm. At populations $<10^4$ individuals/m^2, organism activity was nonuniform, with the worms tending to concentrate in small areas. At populations $>10^5$ individuals/m^2, stable populations could not be sustained during the experimental period without addition of nutrient.

Chemical Redistribution and Sediment Particle Restructuring. Sediment cores (10–20 g) were collected from each microcosm prior to the start of gaseous purge to establish initial chemical concentrations and whole sediment characteristics (i.e., volumetric water content, organic carbon content, etc.). In addition, sorption partition coefficients and desorptive chemical release kinetics were measured on the parent sediment. See Karickhoff et al. (*5*) for partition coefficient measurement and sediment characterization methods and Karickhoff (*6*) for kinetic release measurement.

Upon termination of each microcosm experiment, "discrete" zones (i.e., fecal layer, sand sublayer, biologically unworked sediment) were sampled individually and characterized with regard to the aforementioned chemical and sediment properties. Periodically, fecal pellets were removed during an experiment and the chemical content and chemical release kinetics determined. Chemical release from "intact" pellets was followed by dispersing fresh pellets (no worms) over a flat surface (not exceeding a single pellet thickness) and measuring the kinetics of release into the water under continuous sparging. The glass bottles and air purge/trap assemblies described previously for the microcosms (Figure 1) were used for these measurements. Chemical release from suspended pellets was followed by gaseous stripping of pellet suspensions in smaller purge cells (≈250 mL volume) with fine glass frit bottoms (Figure 1). Gas flow was routed upward through the cell bottom to keep the pellets suspended.

Chemical Recovery and Analysis. Test chemicals removed by air stripping were trapped on tenax resin columns. Collection columns were changed periodically—the sampling frequency was determined by the anticipated temporal properties of the process(es) in question. Highly purified laboratory air was used as the purge gas. The air was collected (oilless compressor), cleaned (brass frit, paper filter, charcoal, tenax resin), and flow regulated in three stages To avoid cummulative loss of water from purge vessels, purge air was saturated with water and/or makeup water was added periodically. Sparged chemicals were recovered from the resin columns by reverse flow solvent elution (1 pore volumen of acetone followed by 2 pore volumes of isooctane). Water was added to the eluate to remove the acetone, and the test chemicals were quantified in the isooctane phase by electron capture gas chromatography (Tracor 222 GC, SE-30 Gas Chrom Q column).

The test chemicals were extracted from sediment and fecal material with a mixed solvent system consisting of

distilled water, acetonitrile, and isooctane (6:1:1 v/v). Samples were sonicated for 8 h (Cole Palmer ultrasonic bath) with vortex mixing every 2 h. The test chemicals were quantified in the isooctane phase by GC as given above.

The test chemicals in aqueous phase samples were extracted with an acetonitrile/isooctane mixture (1:1), vortex mixed, sonicated for 2 h, and quantified as given above.

Results

Sorption of Hydrophobic Pollutants. Sorption equilibrium is typically characterized by an isotherm, which is a plot of pollutant concentration in the sorbed state (denoted S, expressed relative to dry mass sediment) vs. pollutant concentration in solution (C, expressed relative to aqueous phase volume). For hydrophobic pollutants at typical environmental concentrations (low ppm or less), sorption isotherms approximate linearity and can be described by ($S = K_pC$) where K_p is the equilibrium partition coefficient. By convention, concentration units are chosen with the volume element in solution equivalent in mass to the mass unit for sediment; typical units for K_p are therefore liters per kilogram or milliliters per gram. previous sorption studies with hydrophobic chemicals similar to those used in this study showed that sediment/water partitioning of a given compound on different sediments is highly correlated with the organic carbon content of the sediment (*7*). Partition coefficients normalized to organic carbon (denoted K_{oc}) were found to be fairly independent of sediment ($K_{oc} = K_p$/o.c.) where o.c. is the weight fraction of organic carbon in the sediment. K_{oc}'s for the test compounds on whole sediments were determined to be 80 000, 40 000, and 30 000 for hcb, pcb, and tfn, respectively.

Molecular Diffusion Attenuated by Sorption. Under the experimental conditions employed in the microcosms whereby the chemicals were initially distributed uniformly in a semiinfinite sediment column and subsequently stripped continuously from the overlying water, the pollutant flux out of the sediment, F (at time t), is given by

$$F(\text{mass/time}) = \frac{m}{l}\left(\frac{D}{t}\right)^{1/2} \qquad (1)$$

where m is the total mass of the chemical initially incorporated in the sediment to depth l and D is the diffusion coefficient for the pollutant in bottom sediment (*8*). For nonconservative chemicals that degrade uniformly within the sediment zone contributing to interfacial transport (describable by a first-order rate constant, k_d), the flux into the water is given by

$$F(t) = \frac{m}{l}\left(\frac{D}{t}\right)^{1/2} \exp(-k_d t) \qquad (2)$$

Pentachloro- and hexachlorobenzenes showed no measurable degradation over the 3–4-month purge experiments. Flux out of sediments with no oligochaetes was diffusion controlled and conformed to eq 1 (Figure 2) with effective diffusion coefficients of 10^{-4}–10^{-3} cm^2/day. Trifluralin, however, did degrade significantly in the sediment "blanks", and the flux out of the sediments conformed to eq 2. Degradation rate constants derived from purge data (0.005–0.008 day^{-1}) were generally a factor of 2–4 smaller than rate constants inferred from mass-balance deficit determined at the termination of the experiment. This suggests, perhaps, that tfn degraded more slowly in the near-surface zone contributing to purge release than at depth in the sediment. The diffusion coefficients for

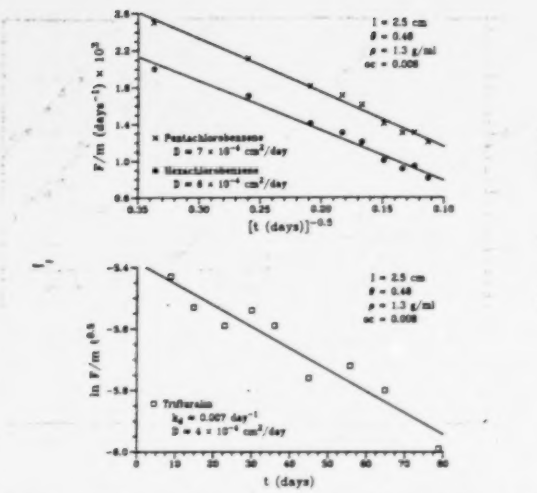

Figure 2. Diffusion-mediated chemical release from bottom sediment in absence of benthic organisms (microcosm 1, blank for microcosm 3).

tfn were in the same range as those observed for the chlorinated benzenes.

As expected, diffusive release of these chemicals is highly retarded by sorption. During a 90-day purge, only the top 1–3 mm of sediment was "stripped" of chemical. A characteristic time for diffusive movement of these chemicals is months per millimeter. Although it is doubtful molecular diffusion of highly sorbed chemicals will mediate transport directly at the sediment/water interface, this process may redistribute chemicals at depth in the sediments (in the absence of other transport mechanisms) and thus may control the long-term transport behavior.

If sorption equilibrium within the bottom sediment is assumed, apriori estimates of the pollutant diffusion coefficients can be made (*9*).

$$D = \frac{D_0\tau}{1 + K_p\rho/\theta} \qquad (3)$$

θ is the volumetric water content, which varies from 0.3 to 0.8 but was 0.5 for the sediments used in this experiment; ρ is the sediment mass per unit total volume of sediment, which is 0.5–1.8 g/mL; D_0 is the bulk water diffusion coefficient of the pollutant, which is typically (5–10) × 10^{-6} cm^2/s for organic pollutants; τ is the sediment complexity number (in this case, largely tortuosity and porosity), which is close to unity for bottom sediments (*9*). As described previously, the sorption partition coefficient can be estimated from the organic carbon content of the sediment ($K_p \approx K_{oc} \times$ o.c.). For the chemicals and whole sediments used in these experiments (with K_{oc}'s of 10^4–10^5 and organic carbon contents around 1%), one would expect D to be in the range observed, that is, 10^{-4}–10^{-3} cm^2/day.

The molecular diffusion experiments did not reveal nonequilibrium sorptive effects. This does not necessarily indicate the existence of true sorptive equilibrium during transport, but a lack of kinetic resolution to isolate such an effect.

Tubificid Oligochaetes: Impact on Pollutant Transport. Tubificids burrow in surfacial sediments (typically 2–10 cm), ingest sediment fines (silt and clay particles), and egest them at the sediment/water interface as sand-sized cylindrical fecal pellets (*10*). Sorbed pollutants are transported by default in this feeding process *irrespective of the relative pollutant fugacities in the*

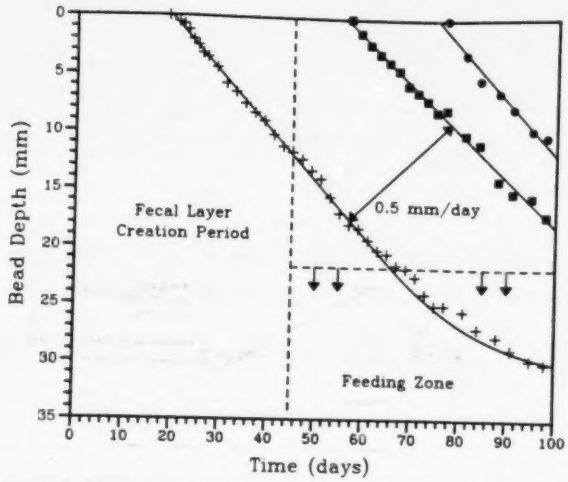

Figure 3. Measurement by glass bead burial of sediment transported by tubificids (microcosm 3, population 4×10^4 individuals/m^2).

system. If the flux of fecal pellets to the surface is denoted F_s, then the pollutant flux (via sediment movement) is given by the product $F_s S^f$, where S^f denotes the sorbed pollutant concentration on the *transported* sediment. The pollutant flux into the water, F_p, can be expressed as

$$F_p = F_s S^f R \tag{4}$$

where R describes the pollutant release from the fecal pellet during its residence time at the surface. In the absence of other benthic organisms and/or turbulence that produces stirring or scouring of surface pellets, the residence time (and thus R) is directly related to pellet flux, F_s.

Sediment Transport (F_s). In this study, sediment transport derives solely from tubificid activity and is assumed to be independent of the presence of pollutants. Worm activity is typically quantified in terms of fecal pellet depositional rate and maximum depth worked by the organisms. Recently, Fisher et al. (*11*) and Krezoski et al. (*9*) used an advective feeding model to describe oligochaete feeding; the approach used herein is patterned after these models.

When the worms were introduced into microcosms containing hcb, pcb, and tfn equilibrated with whole sediments, they began pumping the *sediment fines* (composited into fecal pellets) to the surface. The pumping of "virgin" sediment (previously unprocessed by the worms) continued for 30–50 days in different microcosms. During this period, the sediment, which was initially well mixed, became stratified—a surface zone of fecal material and a sublayer of sand (depleted of fines), highly perforated with worm burrows. Toward the end of this period, the microcosms approached a steady-state condition, in terms of sediment stratification, wherein some portion of the fecal material was reprocessed and "recycled". During this latter period, worm activity declined sharply below the fecal zone and was limited to the larger worms in the population.

The rate and depth dependence of worm feeding were followed by periodically introducing fluorescent glass beads onto the sediment surface and observing their subsequent burial on the edges of the microcosms (Figure 3). In systems where worm populations were stable throughout the experiment, bead burial rates showed no significant dependence upon time of introduction. Also, the beads descended at a fairly constant rate through at least half of the eventual depth of the fecal pellet zone, indicating that the major organism feeding was below this "near-surface" portion of the fecal layer (for example, below 2 cm for the microcosm described by Figure 3). This finding is significant because it suggests discrete "turnover" of the fecal layer. The turnover interval (τ_r) for fecal material was defined to be the time required for the glass beads to reach the midpoint of the *feeding* zone, which varied from 40 to 70 days in different microcosms.

Table I. Sediment Physical Properties: Effect of Tubificids–Microcosm 3 (Population 4×10^4 Individuals/m^2)

	whole sediment	fecal layer
volumetric water content (θ)	0.48	0.80[a]
solids concentration (ρ)	1.25	0.52[a]
organic carbon fraction (o.c.)	0.008	0.028[a]
hcb concentration, ppm	0.96	3.6[b]
pcb concentration, ppm	1.0	3.3[b]
tfn concentration, ppm	1.2	0.5[b]

[a] Determined at termination of run (day 90). [b] Determined on fresh fecal pellets collected on day 29.

Pollutant Concentration (S^f). During the period of fecal layer creation, the effect of particle sorting on pollutant concentration was clearly evidenced (Table I). Pollutant concentration in the fecal material relative to the whole sediment is given by

$$\frac{S^f}{\bar{S}} = \frac{K_p{}^f}{\bar{K}_p} \tag{5}$$

where the bar denotes whole sediment values and the superscript f denotes fecal material. For hydrophobic chemicals, this enhancement ratio can be expressed in terms of the relative organic carbon content of fecal material vs. the whole sediment.

$$\frac{S^f}{\bar{S}} = \frac{K_{oc}{}^f \text{o.c.}^f}{\bar{K}_{oc}\overline{\text{o.c.}}} \approx \frac{\text{o.c.}^f}{\overline{\text{o.c.}}} \tag{6}$$

For the conservative test chemicals (pcb and hcb), there was a 1:1 correspondence between organic carbon redistribution (i.e., $\text{o.c.}^f/\overline{\text{o.c.}}$), and chemical redistribution in all microcosms (correlation coefficient = 0.94, 12 microcosms). In every case, the vast majority (i.e., >90%) of the test chemicals in the biologically worked zone was incorporated into fecal material and transported to the sediment surface. A rough estimate of pollutant redistribution can be derived by assuming *all* the chemical in the "worked" zone ends up in fecal material or

$$S^f \approx \bar{s}/f_{\text{fecal}} \tag{7}$$

when f_{fecal} is the fractional mass of the whole sediment that is processed by the worms.

A characteristic rate for chemical movement (via sediment pumping) with worm populations around 5×10^4 individuals/m^2 was millimeters per day. For highly sorbed chemicals of the type used in these experiments, diffusive transport in fecal layer pore water (from eq 3, with o.c. $\approx$ 0.02–0.05, θ = 0.7–0.8, $\rho \approx 0.7$) is roughly 2 orders of magnitude less than sediment-mediated transport. Even given substantial enhancement of pore water movement effected by worm activity, sediment transport will still dominate chemical movement.

In addition to redistributing the test chemicals, the presence of the worms significantly altered the reactivity of tfn. In blank microcosms (no worms), tfn showed half-lives of 20–30 (subsurface) and 60–80 days for near-surface environments. With the introduction of worms,

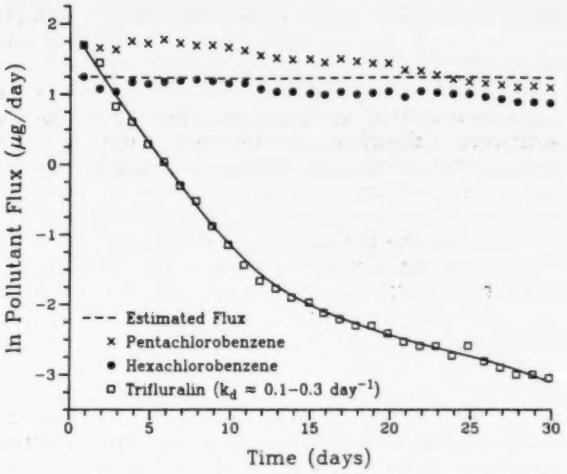

Figure 4. Oligochaete-mediated pollutant release–purge release from microcosm 3 (population 4 × 10^4 individuals/m^2).

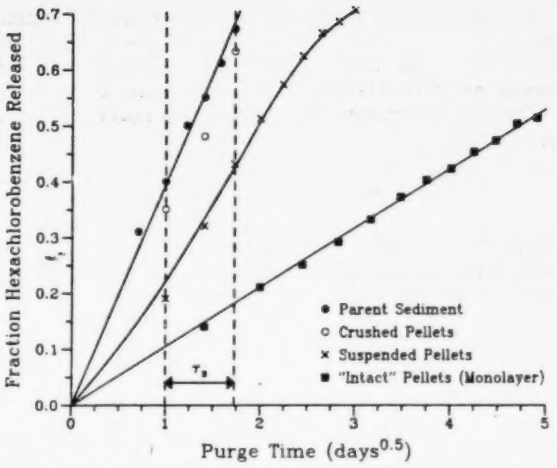

Figure 5. Release of chemicals from fecal pellets (pellets taken from microcosm 3 on day 29).

however, the tfn concentration in fresh fecal pellets decreased exponentially (half-life 2–4 days) during the period of fecal layer creation. Trifluralin flux into the water during this period reflected an equivalent decay (see Figure 4). Once the fecal layer was formed and "recycling" commenced, however, tfn showed very minimal decay (half-life >60 days). Willis et al. (*12*) observed similar behavior for tfn in bacterial suspensions, which they attributed to microbially mediated chemical reduction, where the organisms induced a drop in E_h sufficient to chemially reduce tfn.

Pollutant Release from Fecal Pellets (R). Pollutant release from intact fecal pellets is via molecular diffusion and, for hydrophobic chemicals, is highly retarded by sorptive interactions with the pellet material. Purge-induced release of the test chemicals from fresh pellets (distributed as a disperse monolayer) in the absence of worms showed that times of the order of a month were required for release of half the hcb and pcb contained in the pellets (see Figure 5). Suspending the pellets enhanced the release, primarily as a result of induced pellet fracturing. After extensive sonication (30 min in a sonicator), the pellet material appeared completely dispersed and release rates approached those characteristic of the unpelletized parent sediment. Since in the microcosms the pellet residence time at the surface (τ_s) is characteristically short compared to the time scale of chemical release from intact pellets, diffusive release can be treated in the "short time" limit, whereby the fraction of the chemical released from the pellet during the period τ_s (denoted $f(\tau_s)$) is given by

$$f(\tau_s) = k_t^f(\tau_s)^{1/2} \qquad (8)$$

where k_t^f is the effective diffusive release coefficient for intact pellets that incorporates physical characteristics of the pellet and the diffusion coefficient for the pollutant in the pellet.

This equation assumes continuous purge of the released chemical from the water column and a uniform initial distribution of the chemical in that portion of the pellet contributing to release during this period. In addition, a planar source is assumed, which ignores any complex surface geometry of the pellet. These conditions seem plausible for fresh pellets during their brief period of surface exposure.

In the microcosms, these surface residence times were equated *operationally* with the mean "lifetime" of the fluorescent beads on the surface, which varied from 1 to 3 days. (This lifetime was dependent solely on the sediment flux and for different microcosms was approximately 0.5 mm/F_s with F_s expressed as millimeters per day.) Figure 5 shows that hcb release from intact pellets follows the prescribed temporal behavior (eq 8) for times well in excess of "measured" values of τ_s. For pellet residence times at the surface of 1–3 days, one would expect a 10–20% loss in the three test chemicals. Insufficient data (in terms of different chemicals and different sediment sources) were collected to evaluate the variability of k_t^f. It should be indicated, however, that one would expect an inverse relationship between k_t^f and the equilibrium partition coefficient, K_p. That is, any change in sediment properties that enhanced sorption (i.e., increased organic carbon content) would further retard chemical release. Likewise, more hydrophobic chemicals would be sorbed more strongly and, therefore, be released more slowly than those described herein. Also, it should be pointed out that fecal pellet stability (and therefore the chemical release coefficient, R) in a field situation will be impacted by the activities of other benthic organisms and dimersal fishes, which were not present in these microcosms. The diffusion component $f(\tau_s)$ should be considered a lower limit for the release coefficient, R.

Pollutant Flux from the Microcosms. Under continuous sparging of the water column, the pollutant flux into the water during the period of fecal layer creation was fairly constant for pcb and hcb, as given by

$$F_p = F_s S^f R \approx F_s \frac{\text{o.c.}^f}{\overline{\text{o.c.}}} \bar{s} f(\tau_s) \qquad (9)$$

where again the bar denotes whole sediment values. In these experiments, F_s and τ_s were determined from bead burial, and o.c.^{f}, $\overline{\text{o.c.}}$, and $f(\tau_s)$ were measured independently on samples extracted from the microcosms; this enables an *independent* estimate of F_p and, thereby, provides a check on the process factoring of eq 9. For example, in microcosm 3 (see Table I and Figures 3–5)

$$F_s = 0.05 \text{ cm/day} \times 250 \text{ cm}^2 \times 0.52 \text{ g/cm}^3 = 6.5 \text{ g/day}$$

$$\text{o.c.}^f = 0.028 \qquad \overline{\text{o.c.}} = 0.008$$

$$\bar{s} = 1.0 \text{ ppm (pcb)}, 0.96 \text{ ppm (hcb)}, 1.2 \text{ ppm (tfn)}$$

$$\tau_s \approx 2 \text{ days}; f(\tau_s) \approx 0.15 \text{ for } \tau_s = 2 \text{ days}$$

The estimated pollutant flux would be about 3.5 μg/day for each chemical, which corresponds closely with that observed for pcb and hcb during the fecal layer creation period and with the initial tfn flux (Figure 4).

For nonconservative chemicals, in this case tfn, the flux is given by

$$F_p = F_s \frac{\text{o.c.}^f}{\overline{\text{o.c.}}} \bar{s} f(\tau_s) \exp(-k_d t) \quad (10)$$

where k_d describes the degradation, assumed to be first order and uniform in the zone contributing to sediment flux. As indicated previously, this degradation rate constant was 0.2–0.4 day^{-1} in the presence of worms.

Subsequent to fecal layer creation, pollutant flux out of the microcosms decreased fairly continuously (for the duration of the experiments, ~90 days), and fitted reasonably well to a first-order decay function with rate constants of 0.01–0.03 day^{-1} for the three test chemicals. If one assumes repetitive cycling of fecal material with some chemical fraction, $f(\tau_s)$, lost to the water during each successive turnover (period τ_r)

$$F_p \approx F^0 \exp[-f(\tau_s)t/\tau_r] \quad (11)$$

where F^0 is the flux during fecal layer creation. If $0.1 < f(\tau_s) < 0.2$ for each turnover, and τ_r = 30–60 days, the estimated decay constant is approximately 3×10^{-3} day^{-1}, which is somewhat smaller (3–10-fold) than observed. The independent measurements of sediment turnover (bead burial) and pollutant release (pellet monolayer purge) did not indicate dramatic changes during this recycle period, so the cause for the enhanced decay in chemical flux was not elucidated.

An obvious change in chemical behavior during fecal layer recycle was the abated tfn decay, which now approximated decay in the surface zone of the blank microcosms ($k_d \approx 5 \times 10^{-3}$ day^{-1}) with no worm effect.

Conclusions

The transport of hydrophobic pollutants in bottom sediments in the presence of oligochaete worms was contrasted with transport via molecular diffusion. In microcosms containing stable worm populations ($10^4 - 10^5$ individuals/m^2) pollutant transport within the biologically worked surfacial sediment was entirely worm mediated. Sorbed pollutants were redistributed and/or cycled within the fecal zone in accordance with the life habit of the organism(s), irrespective of pollutant fugacity. Sediment was pumped in a generally vertical direction at rates of 0.3–1.0 mm/day, dependent primarily upon worm population and size. This compared to maximal pollutant diffusion rates of a millimeter per month for highly sorbed chemicals of the type used in these experiments.

The discharge of pollutants out of the sediment into the water (under continuous stripping) was enhanced substantially by the presence of the worms (4–6-fold increase over a 90-day period), but not orders of magnitude as might be expected from the enhanced chemical transport within the sediment profile. The mitigating process appeared to be sediment pelletization by the worms, which "entraps" the sorbed chemical and significantly retards chemical release into the aqueous phase. For the hydrophobic chemicals studied, less than 20% of the chemical contained in an intact pellet was released during a characteristic pellet lifetime at the surface (which was 1–3 days). Chemical release was enhanced by pellet fracturing, but in these microcosms, appreciable pellet fracturing occurred only at depth in the sediment and did not appear to contribute to chemical release into the water.

This study substantiated the intimate link between oligochaete activity and pollutant movement in bottom sediments. Although no effort was made to integrate (with worm activity) other pollutant transport processes operative in a field situation, several inferences can be drawn regarding oligochaete impact on pollutant transport.

Over short time periods (days to weeks) the presence of oligochaetes can expand considerably the depth of sediment "interacting" with the water column. Pollutants can be transported to (or from) depths of up to 10 cm in this time period. Redistribution of highly sorbed chemicals within the biologically active layer is via sediment movement, which in large part derives from benthic organism activity. An important facet of this behavior is that the time required for hydrophobic pollutant mixing in this zone is relatively independent of pollutant physical properties and pollutant fugacity. Hexachlorobenzene, pentachlorobenzene, and trifluralin are "mixed" at the same rate. Pollutant exchange at the water/sediment interface is "driven" by the fugacity differential between the surface sediment and overlying water. The kinetic exchange coefficient is the sediment turnover rate modified by a release factor (such as R in eq 4) that compensates for chemical release or uptake retardation due to sediment pelletization.

Pollutant transport below the fecal zone is typically controlled by molecular diffusion. For "long-lived" pollutants, this process may rate limit chemical uptake and release over long periods of time (months to years).

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